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Structural diversity of interaction products of mucochloric acid and its derivatives with 1,2-ethanedithiol

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ABSTRACT

The synthesis and characterization of previously unknown sulfur-containing products from the reaction of mucochloric acid (3,4-dichloro-5-hydroxy-2(5*H*)-furanone) and its 5-alkoxy derivatives with 1,2-ethanedithiol is reported. Under basic and acidic conditions both SH-groups of the reagent show nucleophilic activity, leading to the formation of substitution products of different structural types. Novel fused (7-hydroxy-2,3-dihydro[1,4]dithiino[2,3-*c*]furan-5(7*H*)-one) and spiro (9-chloro-6-methoxy-7-oxa-1,4-dithiaspiro[4.4]nonan-8-one) bicyclic compounds, as well as various bis-thioethers have been obtained and characterized by NMR spectroscopy and single crystal X-ray diffraction.

1. Introduction

2(5*H*)-Furanone derivatives are naturally occurring and extremely useful heterocyclic compounds in various branches of medicine, agriculture, technology, and organic synthesis.[1] One of the most important representatives of unsaturated γ-lactones is mucochloric acid **1** (3,4-dichloro-5-hydroxy-2(5*H*)-furanone), well-known as a commercially available starting material with a range of reactivity.[2] Due to the propensity of compound **1** for cycle-chain tautomerism[2,3] (Fig. 1) and the presence of different reaction centers, this heterocycle is widely used as a versatile building block for the preparation of a variety of interesting compounds.

Despite the large number of publications devoted to reactions of **1** and its derivatives with *O*-, *N*-, *C*-, and *P*-nucleophiles, the reactivity toward sulfur-containing reagents is scarcely explored.[4–8] Recently, in connection with our ongoing projects related to the synthesis and investigation of the structure and properties of sulfur- and selenium-containing derivatives of chemically and biologically active heterocycles, we have studied reactions of **1** and some of its ethers and thioethers with various thiols,[9–11] and selenophenols.[12] It was shown that by conducting reactions of **1** with thiols under basic or acidic conditions it is possible to selectively introduce different SR groups into specific positions of the γ-lactone ring (atoms C(3), C(4), and C(5)) and to obtain pure regioisomers of thioethers of the 2(5*H*)-furanone series.[9,12]

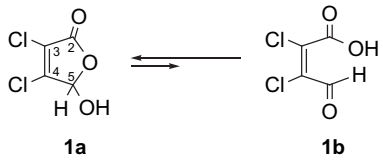

Fig. 1. Cycle-chain tautomerism of mucochloric acid **1**.

In a further effort to reveal the potential of **1** as a useful building block for the synthesis of new sulfur heterocycles, we initiated a study into the reactivity of **1** toward sulfur-containing

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